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## THERMAL BEHAVIOUR OF PERFLUOROPOLYETHER W/O PERCOLATIVE MICROEMULSIONS

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### Abstract

The thermal properties of a perfluoropolyether (PFPE) W/O microemulsion were investigated by Differential Scanning Calorimetry (DSC) both on freezing the liquid samples and upon their melting. PFPE systems as a function of increasing volume fraction ( $\Phi$ =water+surfactant/total), were studied along a dilution line with a water/surfactant molar ratio W/S=11. The percolative nature of these systems emerged directly from the spreading of the exothermic peaks associated with the freezing of the dispersed phase. This behaviour was found to depend on whether the starting temperature of the DSC measure was at, below or above the percolative threshold temperature of the given sample. A low temperature 'needle-like' peak was found around 143 K, immediately after the glass transition due to the oil continuous phase. The low temperature peak was also present in other percolative, three-component microemulsions. The higher order phase transition at the percolation temperature was also evidenced.

**Keywords:** DSC of percolative microemulsions, fluorinated compounds, free water, higher order phase transitions by thermal analysis

### Introduction

In this paper we report, for the first time, about a study of the thermal properties of fluorinated water-in-oil microemulsions by DSC.

The ternary system consisting of a perfluoropolyether (PFPE) oil (O), a PFPE surfactant (S) and water, shows at  $T=293$  K a large monophasic domain of homogeneous transparent and isotropic samples [1]. The physical and structural properties of the above system were characterized by phase diagram [1], electrical conductivity measurements [2], dielectric spectroscopy analysis [3], light scattering [4], small angle neutron scattering (SANS) [5-6] and nuclear magnetic resonance investigations [7-8].

DSC was applied for the first time to non-percolative four-component microemulsions by Senatra *et al.* in 1984 [9]. Recently the above procedure was extended to three-component percolative W/O microemulsions [10] with the purpose of evidencing the higher order phase transition associated with the percolation phenomenon occurring in the liquid microemulsion state of the samples. The amount of information that the DSC approach offers is summarized hereafter.

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### DSC of non percolative W/O microemulsions

i) First order phase transitions associated with the melting of previously frozen samples, confirm that the two main components of these systems, namely, water and oil, do behave as true massive phases, by melting at the melting temperatures of each one of the two pure compounds [11–12].

ii) The enthalpy values associated with the water endotherm, allow the evaluation of the free water fraction as well as of the amount of water bound to the hydrophilic groups of the surfactant. In the case of the oil, if the surfactant is insoluble in the oil, then the enthalpy evaluated from the oil melting endotherm confirms that all of the oil contained in the sample has melted. If the surfactant is partly soluble in oil, as for the water component, the evaluated enthalpy offers an estimate of the percentage of free oil as well as of the amount of oil trapped in the surfactant hydrophobic tails.

iii) The thermal analysis of microemulsions was [12] also found very useful for distinguishing between different forms of water, as well as, for studying the properties of water confined in low dimensionality environments [13–14].

iv) The study of the freezing exotherms of microemulsion systems was undertaken to the purpose of analyzing the behaviour of water in low dimensionality environments. In fact it was found that the free water fraction of the sample maintains its liquid state down to temperatures near the homogeneous nucleation temperature of water, without requiring a quenching procedure, with applied thermal rates as low as  $0.1 \text{ K min}^{-1}$  [11, 15].

v) The study by DSC of the freezing behaviour of microemulsion samples has shown that, for a given sample at a given scan speed, the freezing temperatures of both the water and the oil depend neither on the temperature at which the freezing study began nor on the thermal history of the sample.

### DSC of percolative microemulsions

i) As far as first order phase transitions is concerned, the melting spectra of percolative W/O microemulsions follow the same behaviour described for not-percolative samples.

ii) With regard to the freezing spectra, recent findings [10] have shown that the results reported in point (v) do not exactly apply to percolative samples: a spreading in the exothermic peaks due to the freezing of the dispersed phase was observed depending on the starting temperature of the freezing process.

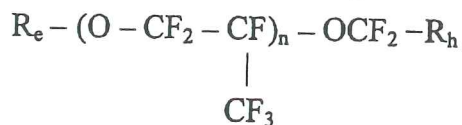
iii) The study of the higher order phase transition due to the percolation phenomenon proved that the above transition depends not only on the starting temperature of the DSC freezing run, but also on the sample thermal history.

## Experimental

### *The PFPE system*

The fluorinated components of the microemulsion are perfluoropolyethers (PFPE) manufactured by Ausimont S.p.A. (Milano-Italy). They are obtained by distillation under reduced pressure of industrial PFPE produced by uv photoinitiated oxidation of perfluoropropene. The compounds have the main properties of fluoro-

carbons with fluorocarbons chain rigidity reduced by etheric bridges (C–O–C), that allow the liquid state up to molecular weights of 10000 or more, increasing also the liquid state thermal range of existence. PFPE compounds have the general formula



where,  $R_e$  and  $R_h$ , oil chain ends, are a mixture of  $-CF_3$ ,  $-CF_2CF_3$  and  $(CF_3)_2CF-$  groups.

The surfactant polar head group  $R_h$  is  $-COO^-NH_4^+$ . The oil (Galden LS/215, Ausimont-Italy) has molecular weight ( $M_w$ ) 900, density  $1.8 \text{ g cm}^{-3}$  and viscosity  $\eta = 6.2 \text{ cp}$ . The surfactant, has  $M_w = 710$  ( $M_w$  distribution of 95% by gas chromatographic analysis). The molecule length is  $13 \text{ \AA}$ . The water was taken from a Millipore Milli-Q-System.

Water and oil are insoluble in any proportion; water and surfactant form liquid crystalline phases [1]; the surfactant and the oil solubilize each other completely at temperatures above 298 K with O/S mass ratios  $\leq 1.8$  and at temperatures above 317 K with higher O/S ratios.

The ternary system water-PFPE oil-PFPE surfactant, shows a large monophasic domain at  $T = 293 \text{ K}$  for a water content less than 17% (mass fraction) and a S/O mass ratio in the range 0.05–4.8. The monophasic domain shrinks toward the S–O side of the phase diagram, as the temperature is risen [1].

The experimental path followed in the present work is the dilution line characterized by the molar ratio  $W/S = 11$ . The hydrodynamic radius of the droplets (by light scattering experiments), is  $R_H = 31 \text{ \AA}$  and the second virial coefficient is  $\alpha = -8$ , showing the presence of attractive interactions in addition to the steric repulsion [4]. A droplet core radius  $R = 16 \text{ \AA}$  and an interfacial area per surfactant molecule of  $50 \text{ \AA}^2$  were evaluated by SANS measurements [5–6].

**Table 1** Composition of PFPE W/O microemulsions

$\Phi$	W S O			$T_p/K^*$
	mass%			
0.205	3.95	14.05	82.00	$305.5 \pm 0.2$
0.327	6.37	22.86	70.77	$292.3 \pm 0.3$
0.395	7.80	27.90	64.30	$289.5 \pm 0.3$
0.462	9.20	33.00	57.80	$285.5 \pm 0.3$
0.501	10.05	36.03	53.92	$282.3 \pm 0.3$

Dilution line  $W/S = 11$ . (\*)  $T_p$  from the  $\sigma(T)$  study of Ref. [2]

The composition of the PFPE microemulsion systems investigated in this study is given in Table 1, where the threshold percolation temperatures evaluated from the  $\sigma(T)$  study are also reported for each sample [2].

### DSC study

The thermal analysis was performed with a Mettler TA 3000 Differential Scanning Microcalorimeter equipped with a low temperature DSC-30 Silver cell. The measuring range ( $dH/dt$ ), in the actual configuration was 17 mW. The standard sensor was set in the high sensitivity position. The temperature interval analyzed extends from 333 down to 93 K. The equipment was modified in order to allow the refilling of the liquid nitrogen Dewar, without removing the low temperature cell, while the TA 3000 unit is on, in a given standby state. In this way the calibration assessment of the calorimetric head is maintained constant [15].

Aluminum pans of equal mass were used for both the sample and the reference. The mass accuracy was of  $\pm 2\mu\text{g}$ . After each measuring run the mass of the sample pan was checked in order to exclude any leakage during the measure. Nitrogen gas of 5.5 purity was used for purging the cell. A flow of  $20\text{ ml min}^{-1}$  was used.

The sample mass in the range 5–10 mg was chosen according to the following requirements: 1) The constant pressure condition must be satisfied in DSC measurements on systems in the condensed state, hence the sample pan cannot be completely filled, because at a higher order phase transition, an expansion of the sample may very likely occur. 2) Samples with components with high enthalpy values (as f.i., for water the enthalpy is  $\Delta H_w = 333.42\text{ J g}^{-1}$ ) if too large, would give output signals that may fall outside the measuring range of the instruments. 3) The samples cannot be too small either, because the thermal event associated with the higher order phase transition would escape detection. Therefore, depending on the system studied and knowing the composition and the enthalpy values of each component, the sample mass must be experimentally assessed to optimize the fulfillments listed in points 1–3.

The following temperature program was applied in the present investigation. Liquid samples were kept isothermally (about 30 min) at a  $T_0$  starting temperature in the neighbourhood of the evaluated percolative threshold temperature  $T_p$  of the given sample; thereafter the heat flow rate ( $dH/dt$ ) as a function of decreasing temperature was recorded during the controlled freezing of the liquid sample down to the final temperature of 93 K. A scan speed of  $2\text{ K min}^{-1}$  was applied. This thermal cycle was called DSC-EXO run. Then, a second isotherm of about one hour was performed at the final temperature reached in the DSC-EXO run. The heat flow rate was recorded by rising the temperature, always with the same thermal rate of  $2\text{ K min}^{-1}$ , to bring the sample back to the liquid microemulsion state. This second thermal cycle was called DSC-ENDO run. The temperature  $T_L$  reached in the DSC-ENDO run, was about 20 K lower than the  $T_0$  temperature.

During the above two DSC runs the thermal events associated with the first order phase transitions were analyzed, namely, the thermal processes during the freezing as well as the melting of the sample.

As a last step, in order to trigger the higher order phase transition associated with the percolation process, a DSC run was performed by applying a thermal rate higher than the one used in both the freezing and the melting measurements. Previous studies have shown that the latter depends on the type of system and, mostly on the type of surfactant used [10]. In the case of PFPE microemulsions a  $4\text{ K min}^{-1}$  thermal rate was applied within the temperature interval from  $T_L$  up to a temperature higher than

$T_p$ , but anyhow within the temperature range of existence of the system as a microemulsion.

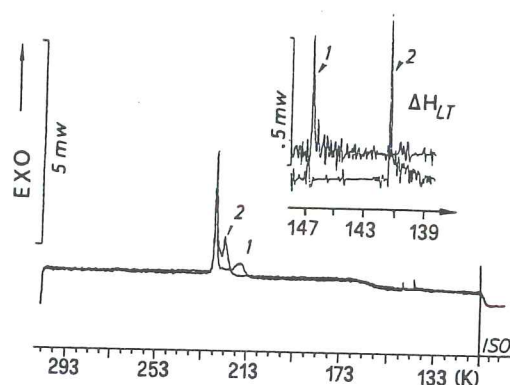
Following the thermal cycle described above, it was possible to control the thermal history of the sample and also to obtain a complete analysis of the thermal properties of the PFPE microemulsions.

## Results

At the present stage of the research the results may be summarized as follows.

### Freezing behaviour

a) PFPE percolative microemulsions, initially kept isothermally at about  $T_p$  and thereafter frozen, exhibit a casual spreading in the exothermic peaks associated with the freezing of the dispersed phase (Fig. 1). The latter conclusion was drawn on the basis of the results obtained by substituting the water with heavy water [9–11] and, by checking that equal amounts of dispersed phase, whether  $H_2O$  or  $D_2O$ , were responsible for the thermal peaks in the DSC-EXO process recorded for samples taken isothermally at different starting temperatures, namely  $T \ll T_p$  and  $T \cong T_p$ . In the former case one obtains a single peak water or heavy water freezing exotherm, in the latter a multi-peaked or a broad distribution of thermal events. The parameter used in the above study was the measured enthalpy (J g of component). These crossed experiments support the interpretation that the above exotherms are due to the freezing of the dispersed phase. Such a behaviour was observed in all the other percolative three component systems listed in Table 2 [10].



**Fig. 1** Freezing exotherms of PFPE microemulsions.  $\Phi=0.205$ . The two curves differ in the temperature at which the sample was taken isothermally before freezing. Curve 1 –  $T_0=304$  K; Curve 2 –  $T_0=294$  K. Note the shift of the peaks linked with the freezing of the dispersed phase and the low temperature 'needle like'  $\Delta H_{LT}$  peak. The latter shifts with temperature opposite to the two main peaks as shown in the enlarged detail

b) The two main peaks in the DSC-EXO spectra are associated with the freezing of the water plus the hydrated surfactant shell. In the freezing exotherms these peaks tend to merge together upon the increase of  $\Phi$  as shown in Fig. 2.

c) In PFPE microemulsions the oil (Galden LS/215 of Ausimont), does not freeze. Therefore the information about the amount of oil frozen and/or melted, is missing;

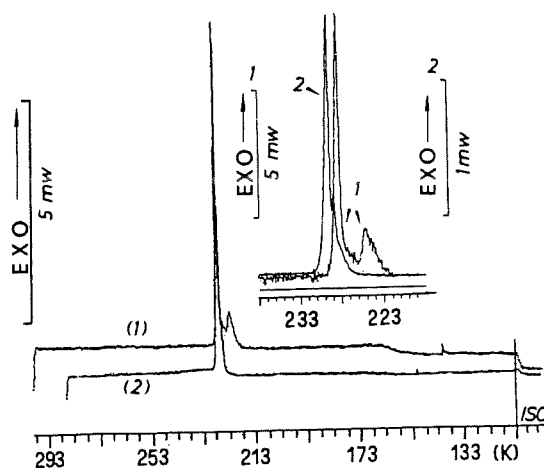
**Table 2** Composition of W/O microemulsions previously tested

System	$\Phi/\text{ml ml}^{-1}$	$W_o/\text{mol mol}^{-1}$	$T_p/\text{K}$
1) $\text{H}_2\text{O}-\text{Na}(\text{AOT})^{(*)}-\text{decane}$	0.35	40.8	300
2) $\text{D}_2\text{O}-\text{Na}(\text{AOT})^{(*)}-\text{decane}$	0.35	40.7	312
3) $\text{H}_2\text{O}-\text{Na}(\text{AOT})^{(*)}-\text{isooctane}$	0.31	37.0	306

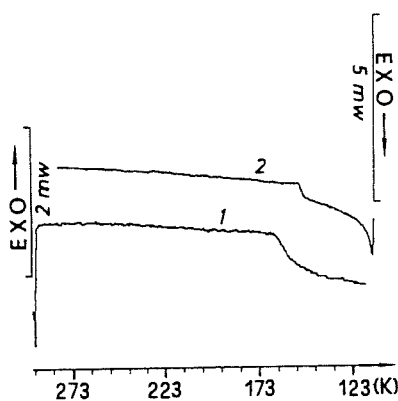
(\*)  $\text{Na}(\text{AOT})$ = sodium di-2-ethylhexyl sulfosuccinate.  $W_o$ =molar fraction (W/S)

moreover it is impossible to evaluate both the amount of oil that behaves as a massive phase and the one 'trapped' between the hydrophobic tails of the surfactant.

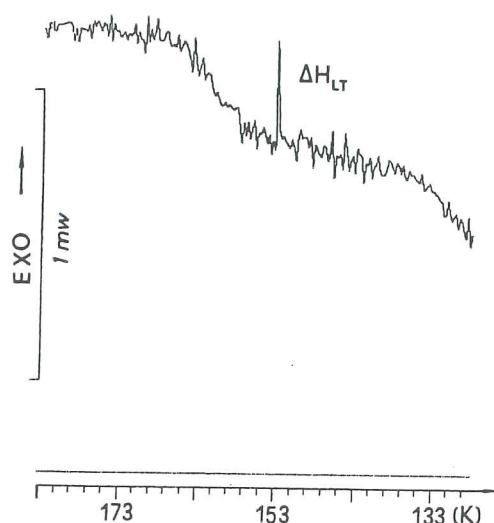
d) The PFPE oil exhibits a glass transition (Fig. 3), which is present in the melting spectra as well as in both the DSC-EXO and ENDO spectra of the microemulsion. The change of the specific heat over the oil glass transition was  $0.235 \text{ J g}^{-1} \text{ K}^{-1}$ .



**Fig. 2** PFPE DSC-EXO spectra. Evolution vs. increasing  $\Phi$ , of the two peaks associated with the freezing of the dispersed phase. Curve 1 –  $\Phi=0.327$ ; Curve 2 –  $\Phi=0.501$ . ( $T \cong T_p$ )  
The processes due to the freezing of the dispersed phase in the temperature range 232–219 K, are drawn in detail

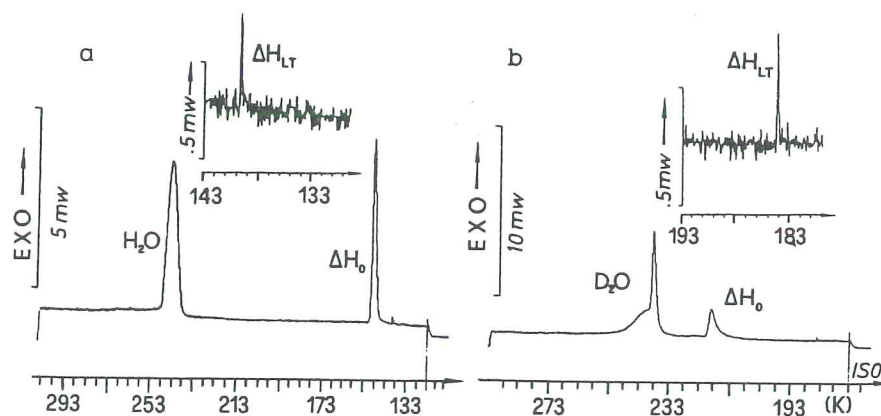


**Fig. 3** Freezing (curve 1) and melting (curve 2) DSC spectra of the oil (Galden LS/215 – Ausimont). The glass transition exhibited by the oil is also observable in PFPE microemulsion samples



**Fig. 4** PFPE W/O microemulsions: a particular of the DSC-EXO spectrum. The low temperature peak, labelled  $\Delta H_{LT}$ , occurs immediately after the glass transition

e) In all the PFPE systems analyzed and listed in Table 1, a low temperature 'needle-like' peak, labelled  $\Delta H_{LT}$  was found to occur immediately after the glass transition (Fig. 4). The latter peak shifts to higher temperatures upon increasing  $\Phi$ . For  $\Phi=0.205$  the low- $T$  peak occurs at 141.6 K and for  $\Phi=0.501$ , at 151.7 K. The  $\Delta H_{LT}$  peak was overlooked in the previous DSC study of percolative microemulsions [10]. Because of the huge thermal events associated with the freezing of the systems massive components, in the direct recordings of the thermal spectra we missed in observing the above low- $T$  peak. A further analysis of the previous data [10] has shown that the  $\Delta H_{LT}$  peak is also present in all the percolative microemulsions there investigated.



**Fig. 5** The low temperature peak  $\Delta H_{LT}$  is also present in all the samples of the W/O microemulsions listed in Table 2. a – System 3; b – System 2. For each sample a close up of the  $\Delta H_{LT}$  peak is also plotted

f) The low temperature event occurs after the freezing of the component with the lowest melting temperature. For sake of comparison, we report in Fig. 5 the DSC-EXO spectra of two of the previously studied [10] percolative microemulsions



namely, a Na(AOT)-heavy water in isooctane and a Na(AOT)-water in isooctane microemulsion. Their composition is given in Table 2.

**Table 3** PFPE microemulsions. Total enthalpic change in the DSC-EXO process

$\Phi$	$\Sigma(\Delta H)_{\text{total}}^*$	$\sigma(\pm)$
0.205	7.110	0.33
0.327	12.284	0.30
0.395	16.953	0.03
0.462	20.644	0.04
0.501	23.047	0.04

\*Values expressed in J/g of sample

g) Along the investigated dilution line, for each composition  $\Phi$ , the total enthalpic contribution ( $\Sigma\Delta H_{\text{total}}$ ) associated with all the thermal events recorded in the freezing exotherms was evaluated. The result is reported in Table 3. It is worth noting that the total sample enthalpy increases with the increase of the system's inter-phase region.

### Melting behaviour

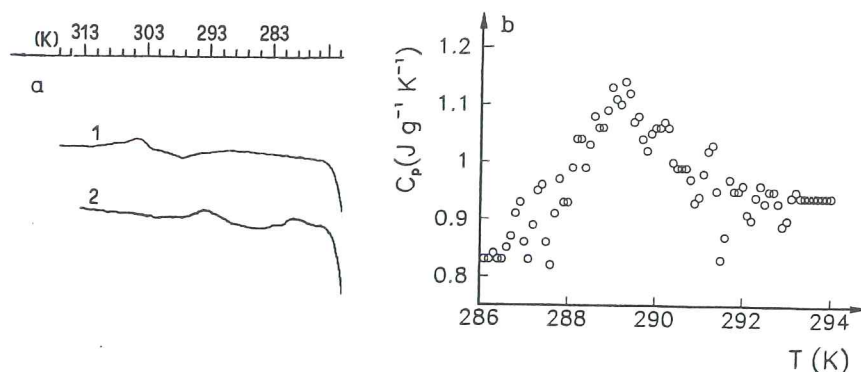
g) In the DSC-ENDO spectra of PFPE microemulsions, besides the glass transition also the thermal event associated with the melting of a free water fraction of the sample was observed. The trend of the free water enthalpy ( $\Delta H_w$ ) along the dilution line W/S=11, for different  $\Phi$ , is reported in Table 4.

**Table 4** PFPE microemulsions. Free water fraction vs.  $\Phi$

$\Phi$	$\Delta H_w^{(1)}$	$\Delta H_w^{(2)}$
0.205	1.91	13.29
0.327	4.92	21.44
0.395	6.58	26.07
0.462	7.12	30.96
0.501	7.76	33.83

$\Delta H$ : J/g of water; (1) experimental values; (2) expected values

h) The higher order phase transition due to the percolation process, was also evidenced for PFPE systems. An example of DSC recordings of the latter thermal event, is plotted in Fig. 6a for two samples with different  $\Phi$  values. The transition temperatures observed by the DSC analysis agree with those evaluated by dielectric spectroscopy and electrical conductivity methods [2]. In Fig. 6b the behaviour of  $C_p$ , after the blank correction, is shown as a function of the temperature for a sample with  $\Phi=0.395$  and  $T_p=289.5$  K. In PFPE samples (Table 1), with  $T_p$  thresholds lower than



**Fig. 6** PFPE microemulsions. The higher order phase transition associated with the percolation process. a – DSC direct recordings. Curve 1 –  $\Phi=0.205$ ,  $T_p=305.5$  K; Curve 2 –  $\Phi=0.327$ ,  $T_p=292.5$  K. b – Evaluation of the specific heat at constant pressure ( $C_p$ ) vs. temperature for the microemulsion sample with  $\Phi=0.395$  and  $T_p=289.5$  K

289 K, the higher order phase transition could not be clearly evidenced. In fact the last DSC run requires a  $\Delta T$  interval extending from  $T_L$  up to a temperature of at least 20 K higher than the evaluated percolation temperature. At the  $4 \text{ K min}^{-1}$  rate, about 20 K are lost in the very first part of the DSC recording. Therefore to measure a transition with  $T_p \approx 264$  K, for instance, one must start the DSC run from 248 K at least! In doing so, there is a competition between two different phenomena, the overcooling and the percolation. As a result the transition by itself becomes difficult to detect because it will fall within the initial stabilization phase of the DSC measure and no evaluation of  $C_p$  would be possible.

## Discussion

The spreading of the exothermic events linked with the freezing of the dispersed phase shown in Fig. 1 for PFPE microemulsions, is in agreement with the results gathered on other percolative three-component systems as reported in [10].

The percolation phenomenon requires a certain concentration of droplets to be reached, only in this condition short range attractive interactions between the droplets may develop: in a very dilute microemulsion, droplets will ignore each other. Under the experimental conditions adopted in this work, by keeping the samples isothermally at  $T \approx T_p$ , droplet-clusters of different size may form. Besides the cluster connecting the system, along maybe a tortuous path as in a maze, (just to help figuring the process), also clusters of smaller size may form, as blind alleys in the maze. Since the droplets have the same radius, the only difference resides in the number of droplets in a given cluster. Upon freezing, the concept of droplets vanishes and water domain will form with the dimension of the clusters. Once verified that in a given sample there is a fraction of water that behaves as free, we believe that the droplets size does not play a fundamental role in the freezing behaviour of percolating microemulsions but, rather, the size of the domain the water forms within the oily environment. The experimental findings so far gathered, support the interpretation that the smaller the cluster is, the lower its freezing temperature will be. The latter seems to

be a general behaviour of percolative microemulsions as it occurs in the PFPE W/O systems here described as well as in the other percolative microemulsions listed in Table 2 [10].

As far as the low temperature  $\Delta H_{LT}$  thermal event is concerned, as a first step we verified whether the latter were a sharp exotherm marking an eutectic temperature. Along the dilution line, the systems are characterized by an increasing number of droplets with the same radius but, they differ in the proportions between the components (Table 1). On freezing, outside the microemulsion state, these systems could behave as mixtures and, therefore, pass through an eutectic point.

A study was performed aiming at investigating the temperature dependence of the  $\Delta H_{LT}$  peak. Each PFPE sample was taken isothermally at a temperature different from the percolative one. Several 'initial' temperatures, in the neighborhood of  $T_p$ , were tested, obviously always within the range of existence of the system as a microemulsion. The samples were thereafter frozen and the DSC-EXO spectra recorded. For any given sample, the  $\Delta H_{LT}$  peak was found to occur at different temperatures, depending on the sample thermal history. An example of the latter investigation is plotted in Fig. 7. However, since an eutectic point must only depend on the sample composition and not on the thermal history the sample went through, the above study allows to exclude the  $\Delta H_{LT}$  peak be an exotherm at an eutectic point.

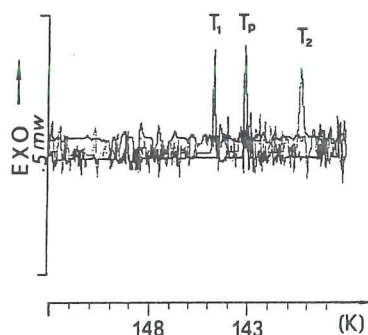


Fig. 7 PFPE microemulsions. The low temperature peak  $\Delta H_{LT}$  occurs at different temperatures depending on the thermal history of the sample. The latter behaviour excludes the peak be due to an 'eutectic' exotherm. Sample with  $\Phi=0.327$ ,  $T_p=292.5$ ,  $T_1=300$  K,  $T_2=288$  K

As a second step, we tried to find out to which component the  $\Delta H_{LT}$  event could be ascribed. For this purpose we report here on the results obtained with a Water-AOT-Isooctane system (Table 2 and Fig. 5a), where all the required information was available. We ought to shift to another system because the PFPE oil of PFPE microemulsion does not freeze as explained in point c) of the previous section.

Following the procedure described previously, for both the oil and the water, a comparison was made between the enthalpy values calculated from the melting as well as the freezing spectra.

In the case of the isooctane oil, within the experimental errors (1%), the same amount of oil was found to be involved in both processes. Therefore it is reasonable to assume that the oil is not responsible for the low- $T$  exotherm. On the contrary, for the water, the same comparison has shown that the enthalpy value  $\Delta H_w$  obtained in the melting process is larger than that measured in the freezing process. In other

words, in the former the 80.7% of the water contained in the sample did melt, in the latter only the 75.5% did freeze, or  $[(\Delta H_w)_{\text{ENDO}} > (\Delta H_w)_{\text{EXO}}]$ . By expressing the enthalpy in J/g of water, we evaluated the enthalpy difference between the two processes, namely  $[(\Delta H_w)_{\text{ENDO}} - (\Delta H_w)_{\text{EXO}}] = 17.257$  (J/g of water). From the latter result we could estimate the amount of water missing in the freezing process.

The measured value of the enthalpy associated with the low temperature peak, measured in J g of sample, was then expressed in J g of 'missing water' according to the relation

$$\Delta H_{\text{LT}} = \frac{\text{measured value} (*) \times \text{sample mass}}{\text{'missing water mass'}} = 17.49 \text{ (J/g of missing water)}$$

(\*)  $\Delta H_{\text{LT}}$  is in J g of sample

The result shows that the latter value, within the experimental errors, agrees with the above enthalpy difference. We recall that the low- $T$  peak, although significant with respect to the signal to noise ratio, is indeed a very small thermal event. The error on the measured enthalpy is therefore rather large (of the order of 4%). The latter value was estimated experimentally, by performing several DSC measurements on different samples with the same composition that is taken from a large sample. Obviously, the amount of missing water as well as the enthalpy of the  $\Delta H_{\text{LT}}$  peak, depend on the water content of the sample and on its composition.

The procedure described was found to apply to all the microemulsion systems listed in Table 2. The above study on percolative water-in-oil microemulsions with no PFPE components, demonstrates that the  $\Delta H_{\text{LT}}$  peak cannot be ascribed to the oil phase but it appears to be linked to the dispersed water phase. As the PFPE oil is more insoluble in water than the hydrogenated oils, it is reasonable to assume that the lack of the oil-enthalpy data in both the melting and the freezing process, does not represent a constrain to the actual subject. Therefore the previous calculation was also performed on the PFPE microemulsions which do exhibit a free water fraction both in the melting and in the freezing spectra with a difference between the amount of melted and the amount of frozen water as for not PFPE microemulsions.

The results of the latter analysis support our previous interpretation. At the present state of the research, the low temperature peak detected in the DSC exotherms of PFPE percolative microemulsions as well as in the DSC-EXO spectra of the systems listed in Table 2, seemed be linked to the water. No hypothesis is advanced about the 'state' of this water. Further research is in progress about the latter argument.

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